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DETERMINATION OF HAZARDOUS ELEMENTS IN SMELTER-PRODUCED SULFURIC ACID

W. H. Hedley, et al

Monsanto Research Corporation

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16. ABSTRACT The report presents results of analyses of potentially hazardous impurities (trace elements) in sulfuric acid produced by non-ferrous smelters. Sulfuric acid samples were obtained from acid plants attached to copper, lead, and zinc smelters. Results of analyses provided by some smelters are also included. Trace elements subjected to qualitative and quantitative determinations in this study include: Pb, Cu, Zn, Hg, As, Cd, Se, Sb, and Be, as well as other elements detected in significant concentrations during screening tests. Based on this analytical data, the report indicates yearly outputs of hazardous trace elements contained in smelter-produced acid for possible consumption in a variety of industries. The report also presents information on analytical methods and procedures used in acquiring the reported data.

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ABSTRACT

The Control Systems Laboratory of the Environmental Protection Agency is presently collecting data to determine whether there are any potentially hazardous impurities in the non-ferrous smelter produced sulfuric acid and if these materials could present a potential threat to vegetation and life at a later time. Therefore, potentially hazardous element composition of the non-ferrous smelter produced sulfuric acid was determined.

There were two aspects to this study (1) to acquire sulfuric acid samples of non-ferrous smelter produced sulfuric acid; (2) analyze the samples by atomic absorption spectrometry for potentially hazardous impurities. Sulfuric acid samples were received from seven plants and were analyzed for trace elements, including lead, copper, zinc, mercury, arsenic, cadmium, selenium, antimony, beryllium, and other elements detected at significant levels during screening tests. Analyses of sulfuric acid were also received from five other non-ferrous smelters.

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SECTION I

OBJECTIVES

The overall objectives of this project were to:

1. Acquire samples of sulfuric acid produced at certain non-ferrous smelters;

2. Subject these samples to a multi-element analytical approach to provide a preliminary indication of trace element concentrations of potentially hazardous impurities;

3. Analyze the samples by atomic absorption spectrometry for potentially hazardous trace elements, including lead, copper, zinc, mercury, arsenic, cadmium, selenium, antimony, beryllium, and other elements detected at significant levels during screening tests; and

4. Define the end uses of the smelter-produced acid, determine how much acid is produced by each company, and calculate the quantity of each element contained in the acid produced on a yearly basis.

SECTION II

SAMPLE COLLECTION

Monsanto Research Corporation (MRC) was to acquire sulfuric acid samples from nine companies that operate seventeen non-ferrous smelter plants. These companies and their plants are listed in Appendix A. All 17 plants were contacted either by telephone or by correspondence to outline the program and to convince their management to participate in the study. Out of these nine companies, six (with seven plants) agreed to supply MRC with sulfuric acid samples from their operations. American Smelting and Refining Company (with five plants) agreed to supply us with only analyses of their sulfuric acid. The remaining plants declined to supply us any sulfuric acid samples.

Each company was requested to supply random samples from their non-ferrous smelter-produced sulfuric acid plants. Companies involved were to supply about a pint of sulfuric acid representing three days of production during the period of one week. In order to avoid contamination, MRC supplied each plant with three acid-washed bottles and a brief sampling procedure. The three samples that were received from each plant were then composited at MRC's Dayton Laboratory for analysis.

SECTION III

SAMPLE PREPARATION AND ANALYSIS

Seven commercial-grade sulfuric acid samples from seven plants comprising three types of non-ferrous smelters were analyzed by atomic absorption spectrometry for 14 elements. The samples are identified in Appendix B. The elements analyzed were dictated either by the work statement for this project or by the results of emission analysis of the samples. A portion of sample was evaporated in a heated graphite electrode. The electrode was then analyzed by emission spectroscopy. Evaporation of the samples in the graphite electrode could have resulted in the loss of more volatile species, such as metal halides. This was not a problem in that ASARCO found less than 1 ppm of chloride in the samples they analyzed. The work statement for the project required analysis by atomic absorption for Pb, Cu, Zn, Hg, As, Cd, Se, Sb,and Be. Pb, Zn, Hg, As, Cd, Se,and Sb cover fairly well the elements that are volatile and have volatile compounds which might be found in concentrated sulfuric acid. The results of the emission analyses are shown in Table 1.

Twenty-five ml of each sample (entire sample shaken to ensure uniformity) was diluted to 100 ml with deionized-distilled water. This operation was performed to permit the aspiration of the diluted samples directly into the flame of a Perkin-Elmer Model 303 atomic absorption spectrometer. The Perkin-Elmer was fitted with a triple slot burner. The elements analyzed in this manner were As, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Se, and Zn. The instrument conditions were standard as set forth in the Perkin-Elmer manual[1] except for Ni, where the 352.4 nm line was used as recommended by Perkin-Elmer for iron-containing matrices, and for Fe, where the 252.7 nm line was

Table 1. SEMI-QUANTITATIVE EMISSION ANALYSES

(ppm by wt)

Impurity	Sample No. 1 St. Joe Lead Smelter	Sample No. 2 New Jersey Zinc Zinc Smelter	Sample No. 3 City Service Copper Smelter	Sample No. 4 Missouri Lead Lead Smelter	Sample No. 5 National Zinc Zinc Smelter	Sample No. 6 Bunker Hill Zinc Smelter	Sample No. 7 Bunker Hill Lead Smelter
Aluminum (Al)	0.032						
Chromium (Cr)	0.93			1.19			
Copper (Cu)	>1.5	0.33	>1.5	>3.0	>1.5	>1.5	>1.5
Iron (Fe)	11.9	4.5	0.76	2.1	3.0	9.2	0.76
Magnesium (Mg)	0.03	<0.005		0.02	0.01	0.01	<0.005
Manganese (Mn)	0.03			<0.03		0.03	
Nickel (Ni)	4.5	0.1	0.92	1.2	1.52	1.2	1.03
Lead (Pb)	0.43			<0.32	0.16	<0.16	0.32
Silicon (Si)	0.43			0.32		0.32	0.32
Zinc (Zn)	4.5		1.52	9.2	4.5	3.04	3.04

Note: As, Be, Cd, Hg, Sb, and Se are at a level that was not detectable by the semi-quantitative emission analysis method used for any of these seven samples.

used due to higher concentrations. (Possible Hg interference of this line is low because of the low sensitivity of Hg in a flame [~10 μg/mℓ]). Hg was analyzed by the now widely accepted cold vapor flamelss method.[2] Sb was determined using a Perkin-Elmer model 303-0849 volatile hydride generator and methods developed by Perkin-Elmer and others.[3,4] Be and Cd were analyzed using a Varian Model 61 carbon rod flameless atomic absorption atomizer power supply and a Model 63 Varian carbon rod head assembly. The micro tube furnace was used in both cases. The micro tube furnace is made of pyrolytic graphite and is sheathed from oxidation at high temperatures by a flow of argon or nitrogen. Extremely high atomization temperatures are obtainable with this furnace (>3000°C).

All standards were prepared from regular atomic absorption stock solutions in matrices matching the sample matrices as far as acid concentration is concerned. Ultrex, ultra high purity acid, sold by J. T. Baker, Co. was used to prepare standards.

Appendix C presents in detail the analytical procedure for analysis of potentially hazardous trace element impurities in concentrated sulfuric acid from non-ferrous smelters.

SECTION IV

RESULTS AND DISCUSSION

Table 2 summarizes the results of atomic absorption spectrometric analysis for potentially hazardous trace metals along with annual production and end uses of sulfuric acid from the seven non-ferrous smelters. The annual production and end uses of sulfuric acid were obtained from the operators of seven non-ferrous smelters. American Smelting and Refining Company (ASARCO) supplied typical analyses of sulfuric acid produced at five of their smelters and these are summarized in Table 3.

A review of the data in Tables 2 and 3 shows fairly good agreement between MRC data and ASARCO for samples from similar plants. Arsenic and selenium data were not reported in Table 2 because their concentrations were below the MRC detection limit. MRC contacted Mr. L. W. Anderson, Superintendent, Analytical Services at ASARCO's Central Research Laboratories. Mr. Anderson graciously agreed to analyze our seven samples via the methods they normally use for arsenic and selenium in concentrated sulfuric acid samples from non-ferrous smelters. The results of these analyses are shown in Table 4. These values are similar to the values reported earlier by ASARCO for their acids. Anderson stated, "These levels of both arsenic and selenium are well below the detection limits by normal flame atomic absorption using EDL (electrodeless discharge lamps). Atomic absorption could possibly be used for these levels of arsenic and selenium using hydride evolution methods." The procedures used by ASARCO for these two analyses are reproduced in their entirety in Section C4.0.

Tables 5and 6 show the pounds of each trace metal contained in the sulfuric acid produced on a yearly basis and analyzed by MRC and ASARCO respectively. The majority of the non-ferrous smelter-produced sulfuric acid is used in fertilizer and ore processing.

Table 2. SUMMARY OF ANALYSIS FOR SULFURIC ACID SAMPLES RECEIVED BY MRC

ANALYSIS RESULTS

(ppm by wt.)

Trace Metals	Sample No. 1 St. Joe Lead Smelter	Sample No. 2 New Jersey Zinc Zinc Smelter	Sample No. 3 City Service Copper Smelter	Sample No. 4 Missouri Lead Lead Smelter	Sample No. 5 National Zinc Zinc Smelter	Sample No. 6 Bunker Hill Zinc Smelter	Sample No. 7 Bunker Hill Lead Smelter	Atomic Absorption Method Used
Beryllium (Be)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	Carbon Rod
Cadmium (Cd)	0.11	0.017	0.001	0.002	0.005	0.005	0.114	Carbon Rod
Chromium (Cr)	3.28	0.28	0.30	2.83	0.39	1.85	0.78	Flame-Air-C_2H_2
Copper (Cu)	0.47	0.11	0.13	0.36	0.14	0.21	0.18	Flame-Air-C_2H_2
Iron (Fe)	167	22	9	124	37	183	52	Flame-Air-C_2H_2
Mercury (Hg)	0.029	0.056	0.046	0.009	2.28	0.20	0.161	Flameless
Magnesium (Mg)	0.21	0.15	0.03	1.33	0.15	1.74	0.22	Flame-Air-C_2H_2
Manganese (Mn)	1.35	0.24	0.15	0.76	0.28	1.35	0.48	Flame-Air-C_2H_2
Nickel (Ni)	1.63	<0.11	0.11	1.68	0.18	0.28	0.37	Flame-Air-C_2H_2
Lead (Pb)	2.78	0.38	0.33	0.48	<0.13	<0.13	2.0	Flame-Air-C_2H_2
Antimony (Sb)	0.032	0.010	0.012	0.018	0.003	0.026	0.02	Hydride Generator
Zinc (Zn)	0.24	1.83	0.05	0.1	0.07	1.1	0.08	Flame-Air-C_2H_2
Annual Acid Production (tons/yr)	70,000	150,000	135,000	50,000	73,500	220,000		
Major End Uses	Fertilizer	Batteries, Plastic & Paper	Fertilizer Textile	Fertilizer	Detergent, Water Treatment	Fertilizer		

Estimated accuracy of analytical procedures used to determine results listed above ±5% or better.

Table 3. SULFURIC ACID ANALYSIS BY AMERICAN SMELTING AND REFINING CO. (ASARCO)

ANALYSIS RESULTS

(ppm by wt.)

Trace Metals	Tacoma, Washington Copper Smelter	Hayden, Arizona Copper Smelter	El Paso, Texas Copper Smelter *	Corpus Christi, Texas Zinc Smelter	Columbus, Ohio Zinc Smelter
Arsenic (As)	0.44	0.08	0.5	0.13	0.03
Cadmium (Cd)	<0.005	NA	NA	0.01	<0.005
Copper (Cu)	0.20	0.28	0.1	<0.06	0.07
Iron (Fe)	51.0	32.3	8.0	11.5	24.2
Mercury (Hg)	0.003	0.010	0.003	0.20	0.16
Manganese (Mn)	0.25	0.38	0.06	0.11	0.15
Nickel (Ni)	0.15	0.48	0.10	0.07	0.08
Lead (Pb)	0.25	1.6	1.0	0.27	<0.07
Antimony (Sb)	0.18	<0.01	<0.1	<0.05	0.12
Selenium (Se)	<0.04	0.04	0.06	0.48	<0.04
Zinc (Zn)	0.06	0.94	0.84	0.14	0.11
Annual Acid Production (tons/yr)	44,000	210,000	168,000	53,000	70,000
Major End Uses	Explosives, Pulp & Paper, Fertilizer	Ore Processing	Ore Processing, Fertilizer	Ore Processing, Petroleum Refining	Ore Processing, Fertilizer

* Also smelt zinc and lead at this plant

Table 4. RESULTS OF ASARCO ANALYSES OF MRC SAMPLES

ANALYSIS RESULTS

(ppm wt.)

Trace Elements	Sample No. 1 St. Joe Lead Smelter	Sample No. 2 New Jersey Zinc Zinc Smelter	Sample No. 3 City Service Copper Smelter	Sample No. 4 Missouri Lead Lead Smelter	Sample No. 5 National Zinc Zinc Smelter	Sample No. 6 Bunker Hill Zinc Smelter	Sample No. 7 Bunker Hill Lead Smelter
Arsenic (As)	0.02	0.12	0.02	0.02	0.03	0.03	0.03
Selenium (Se)	*	<0.02	<0.02	<0.02	0.17	<0.02	0.03

*Sample lost

Table 5. TRACE ELEMENT QUANTITIES IN SULFURIC ACID

Produced on a Yearly Basis

Quantities of Trace Elements in Sulfuric Acid
(lb/yr)

Trace Metals	Sample No. 1 St. Joe Lead Smelter	Sample No. 2 New Jersey Zinc Zinc Smelter	Sample No. 3 City Service Copper Smelter	Sample No. 4 Missouri Lead Lead Smelter	Sample No. 5 National Zinc Zinc Smelter
Arsenic (As)	2.8	36.0	5.4	2.0	4.4
Beryllium (Be)	<0.14	<0.3	<0.27	<0.1	<0.15
Cadmium (Cd)	15.4	5.1	0.27	0.2	0.74
Cromium (Cr)	459.2	84.0	81.0	283.0	57.3
Copper (Cu)	65.8	33.0	35.1	36.0	20.6
Iron (Fe)	23,380.0	6,600.0	2,430.0	12,400.0	5,439.0
Mercury (Hg)	4.1	16.8	12.4	0.9	335.2
Magnesium (Mg)	29.4	45.0	8.1	133.0	22.1
Manganese (Mn)	189.0	72.0	40.5	76.0	41.2
Nickel (Ni)	228.2	<33.0	29.7	168.0	26.5
Lead (Pb)	389.2	114.0	89.1	48.0	<19.1
Antimony (Sb)	4.5	3.0	3.2	1.8	0.44
Selenium (Se)	--	<6.0	<5.4	<2.0	25.0
Zinc (Zn)	33.6	549.0	13.5	10.0	10.3
Annual Acid Production (tons/yr)	70,000	150,000	135,000	50,000	73,500

Table 6. TRACE ELEMENT QUANTITIES IN SULFURIC ACID

Produced on a Yearly Basis

Produced by American Smelting and Refining Co.

(lb/yr)

Trace Metals	Tacoma, Washington Copper Smelter	Hayden, Arizona Copper Smelter	El Paso, Texas Copper Smelter*	Corpus Christi, Texas Zinc Smelter	Columbus, Ohio Zinc Smelter
Arsenic (As)	38.7	33.6	168	13.8	4.2
Cadmium (Cd)	<0.44	NA	NA	1.06	<0.7
Copper (Cu)	17.6	117.6	33.6	<6.4	9.8
Iron (Fe)	4,488	13,566	2,688	1,219	3,388
Mercury (Hg)	0.26	4.2	1.0	21.2	22.4
Manganese (Mn)	22	159.6	20.2	11.6	21.0
Nickel (Ni)	13.2	201.6	33.6	7.42	11.2
Lead (Pb)	22	672	336	28.6	<9.8
Antimony (Sb)	15.8	<4.2	<33.6	<5.3	16.8
Selenium (Se)	<3.5	16.8	20.2	50.9	5.6
Zinc (Zn)	5.3	394.8	282.2	14.8	15.4
Annual Acid Production (ton/yr)	44,000	210,000	168,000	53,000	70,000

*Also smelt zinc and lead at this plant

SECTION V

RECOMMENDATIONS FOR ANALYTICAL METHODOLOGY DEVELOPMENT

As a result of the detailed analytical procedure described in Appendix C, the following investigations are recommended:

1. Development of a solvent extraction procedure for As and Se in concentrated sulfuric acid from non-ferrous smelters. (See Section C3.4.2.1 for description of procedure recommended for investigation).

2. Check a series of samples of each element using the known addition method of analysis. This is done as follows: four aliquots of the samples are taken. The first aliquot is diluted to volume with solvent. The other three aliquots are made to volume using suitable quantities of known standards. Each of the latter three should have different quantities of the element being analyzed.

   Determine the absorbance (or peak height for scale expanded samples) of each of the four solutions. Plot absorbance versus concentration and extrapolate the resulting straight line through zero absorbance. The intercept on the concentration axis gives the concentration of the element in the diluted sample solution.

   This method allows for variations in sample matrix composition and would serve as a cross check on the answers obtained for the sample using a standard curve.

3. A synthetic sample could be prepared with various concentrations of potentially hazardous trace elements. This sample would serve as a check on the accuracy of the methods employed by the analyst.

SECTION VI

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APPENDIX A

List of Smelter Sulfuric Acid Plants

COPPER SMELTERS WITH SULFURIC ACID PLANTS

Smelter	Location
Asarco	Tacoma, Washington**
Asarco	Hayden, Arizona**
Asarco	El Paso, Texas**,†
Phelps Dodge	Morenci, Arizona
Kennecott	Hayden, Arizona
Kennecott	Garfield, Utah
City Service	Copper Hill, Tennessee*

LEAD SMELTERS WITH SULFURIC ACID PLANTS

Bunker Hill	Kellogg, Idaho*
Missouri Lead	Boss, Missouri*
St. Joe	Herculaneum, Missouri*

ZINC SMELTERS WITH SULFURIC ACID PLANTS

Asarco	Corpus Christi, Texas**
Asarco	Columbus, Ohio**
Asarco	Amarillo, Texas***
National Zinc	Bartlesville, Oklahoma*
Bunker Hill	Kellogg, Idaho*
St. Joe	Monaca, Pennsylvania
New Jersey Zinc	Palmerton, Pennsylvania*

---

* Supplied MRC with their sulfuric acid samples
** Supplied only analysis of their sulfuric acid
*** No sulfuric acid plant
† Also smelt zinc and lead at this plant

APPENDIX B

Sample Identification

Sample No.	Type of Smelter	Company	Location
1	Lead	St. Joe	Herculaneum, Mo.
2	Zinc	New Jersey Zinc	Palmerton, Pa.
3	Copper	City Service	Copper Hill, Te.
4	Lead	Missouri Lead (Amex Lead Co.)	Boss, Mo.
5	Zinc	National Zinc	Bartlesville, Ok.
6	Zinc	Bunker Hill	Kellogg, Id.
7	Lead	Bunker Hill	Kellogg, Id.

APPENDIX C

ANALYTICAL PROCEDURE

ANALYTICAL PROCEDURE FOR ANALYSIS OF POTENTIALLY HAZARDOUS TRACE ELEMENT IMPURITIES IN CONCENTRATED SULFURIC ACID FROM NON-FERROUS SMELTERS

C1.0 INTRODUCTION

The samples of sulfuric acid from non-ferrous smelters were screened by emission spectroscopy to establish which trace elements were present in the samples and their approximate concentrations. The samples were then analayzed by atomic absorption spectrometry to quantitatively determine the concentrations of the potentially hazardous trace elements of interest.

C2.0 MULTI-ELEMENT SCREENING ANALYSIS

Samples of concentrated sulfuric acid from three types of non-ferrous smelters; lead, zinc and copper; were screened by emission spectroscopy. Two milliliters of each sample were vaporized by dropwise addition to a heated graphite electrode. The electrodes were heated in a metal plate holder on a laboratory hot plate. When the evaporation was completed, ten milligrams of lithium carbonate was added to each electrode. Standards were prepared by weighing ten milligrams of 0.1%, 0.01% and 0.001% emission standards, containing seventy elements in a lithium carbonate matrix, into graphite electrodes. Sample and standard electrodes were arced using a Spex Industries arc/spark stand with an Applied Research Laboratories (ARL) power supply. Optical emission from the electrodes was passed through a Bausch and Lomb (B&L) dual illuminator to a 1.5-meter B&L grating spectrograph. Emission spectra in the region of 250-350 nm were recorded on a 4" x 10" Kodak photographic plate (Spectrum Analysis Plate, Type #1).

Concentrations of elements found to be present in the samples were determined by visual comparison of emission lines in the samples with emission lines in the standard. An ARL densitometer

was used for the visual comparison. Elements of a potentially hazardous nature found to be present by emission spectroscopy in the samples were then quantified by atomic absorption spectroscopy.

C3.0 ATOMIC ABSORPTION

C3.1 INTRODUCTION

Atomic absorption spectroscopy (AAS) has come to the forefront as an analytical tool for the quantitative determination of trace elements in environmental samples. The advantages of adoption of AAS for analysis of environmental samples include minimal sample preparation, specificity and relative freedom from interferences, usefulness for both low and high concentration of metals, speed, and accuracy. A number of reviews have been written containing information on the basic principle of AAS. The reviews of Kahn[6] and Ramĩrez-Muñoz[7] are excellent sources of background information for AAS.

Most instrument manufacturers of atomic absorption spectrometers supply cookbook manuals outlining basic instrument operating parameters for the various trace metals. In addition, these manuals include specific methodology or references for the determination of the various trace elements in different matrices. The term matrix in this case refers to the gross compostion of the sample, i.e., seawater, ground water, petrochemicals, geological samples, biological samples, or agricultural samples. When methods of analysis for trace elements in a particular type of sample have not been defined, as is the case for concentrated sulfuric acid from non-ferrous metal smelters, the methods must be developed by the analyst to the best of his ability within the time and cost restraints placed by the submitter of the samples. With the information outlined above as

a guideline, the following sections describe analytical procedures for the analysis of specific, potentially hazardous, trace elements in concentrated sulfuric acid samples from non-ferrous smelters by atomic absorption spectroscopy.

C3.2 SAMPLE AND STANDARD PREPARATION

A sample to be analyzed by AAS must in some way be vaporized to give a significant population of atoms in the ground state then passed through a beam of light. Three main devices for producing the vapor needed are a flame, cold vapor generation, and carbon rod atomization. A flame is the most general type of vaporization. The sample is normally nebulized into the flame as an aerosol from an aqueous solution. The nebulizer of our P. E. Model 303 atomic absorption spectrometer will accept acid concentration up to approximately 25%. The concentrated sulfuric acid samples from non-ferrous smelters were diluted to 25% of the origianl concentration with deionized-distilled H_2O so they could be nebulized directly into the flame. Standards and blank were prepared by proper dilution of atomic absorption stock solutions (made by Harleco, 60th and Woodbine Ave., Philadelphia, Penn., 19143) with sulfuric acid to match the matrix (25% sulfuric acid) of the samples. The sulfuric acid used was Ultrex, J. T. Baker, Co. with low trace elements content. The actual analysis of sulfuric acid is given in Table C1.

C3.3 INSTRUMENT OPERATING PARAMETERS

Table C2 is a listing of all of the trace elements analyzed in the concentrated sulfuric acid samples from non-ferrous smelters and the instrument operating parameters for each. The instrument used was a Perkin-Elmer Model 303.[1] The operating parameters listed include: hollow cathode lamp manufacturer (all of the hollow cathode lamps are single element cathode except Cr, Cu, Fe, Mn and Ni which were in one multicomponent lamp);

Table C1. ACTUAL ANALYSIS OF ULTREX SULFURIC ACID SOLD BY J. T. BAKER CHEMICAL COMPANY

Formula: H_2SO_4 FW 98.08	ACTUAL ANALYSIS
Assay (H_2SO_4)	95.3%
Residue after Ignition	1 ppm
Specific Gravity at 60°/60°F	1.84
NON-METALLIC IMPURITIES in parts per million (ppm)	
Ammonium (NH_4)	0.8
Arsenic (As)	0.001
Boron (B)*	0.02
Chloride (Cl)	<0.05
Nitrate (NO_3)	0.2
Phosphate (PO_4)	<0.05
Selenium (Se)	0.2
Silicon (Si)*	0.04
METALLIC IMPURITIES* in parts per billion (ppb)	
Aluminum (Al)	3
Barium (Ba)	<1
Bismuth (Bi)	<1
Cadmium (Cd)	<1
Calcium (Ca)	20
Chromium (Cr)	1
Cobalt (Co)	<1
Copper (Cu)	2
Iron (Fe)	3
Magnesium (Mg)	3
Manganese (Mn)	0.4
Mercury (Hg)	<10
Nickel (Ni)	< 1
Potassium (K)	<10
Sodium (Na)	90
Strontium (Sr)	< 1
Zinc (Zn)	< 1

*Average value for three samples vaporized and analyzed spectrographically (DC-arc, indium internal standard in graphite matrix against commercial standards), reading of lines in 2450-3875 A region; strontium, calcium, and barium determined on a single composite sample, reading at 4078 A, 4227 A, and 4554 A, respectively; key elements found absent are reported as < (less than) the detection limit.

Table C2. ATOMIC ABSORPTION INSTRUMENT OPERATING PARAMETERS PERKIN-ELMER MODEL 303

Element	Hollow Cathode Lamp Mfg.	Lamp Current ma.	Wave Length nm.	Gain	Slit Width nm.	Air Flow ℓ/min.	Acetylene Flow ℓ/min.	Scale Expansion Factor	Noise Suppression
Arsenic (As)	Perkin-Elmer	18	193.7	4.6	2.0	--	--	10	3
Berryllium (Be)	Perkin-Elmer	30	235.0	3.0	0.14	--	--	1	1
Cadmium (Cd)	Westinghouse	12	228.8	1.0	0.2	--	--	3 10	2 3
Chromium (Cr)	Westinghouse	25	357.9	3.0	0.7	26.5	4.8	10	3
Copper (Cu)	Westinghouse	24	324.7	3.9	0.2	25.2	4.2	10	3
Iron (Fe)	Westinghouse	25	252.7	4.5	0.2	25.2	3.9	1	1
Mercury (Hg)	Perkin-Elmer	10	253.6	3.0	0.2	--	--	3	2
Magnesium (Mg)	Perkin-Elmer	12	285.2	1.0	0.7	26.5	4.0	1 3	1 2
Manganese (Mn)	Westinghouse	25	279.5	4.5	0.2	26.5	4.1	3	3
Nickel (Ni)	Westinghouse	25	352.4	3.4	0.2	26.5	4.1	10	2
Lead (Pb)	Perkin-Elmer	30	283.3	1.3	0.7	25.7	4.9	10	3
Antimony (Sb)	Jarrell-Ash	20	217.0	4.8	0.2	--	--	1	2
Selenium (Se)	Westinghouse	14	196.0	4.0	2.0	--	--	10	3
Zinc (Zn)	Perkin-Elmer	15	213.9	2.8	0.7	25.2	4.2	3	3

lamp operating current in milliamps; wavelength used for the analysis in nanometers; amplifier gain potentiometer setting; slit width in nanometers; the air flow rate in liters/minute and the acetylene flow in liters/minute, where these are applicable; scale expansion factor, and noise suppression setting.

C3.4 SAMPLE ANALYSIS METHODS

C3.4.1 General Atomic Absorption Analyses

Cr, Cu, Fe, Mg, Mn, Ni, Pb, and Zn were analyzed in the concentrated H_2SO_4 samples using an air-acetylene flame by nebulizing the dilute samples described in section C3.2 directly into the flame. The calibration curves for Cu, Mn, Pb and Zn are shown in Figures C1, C2, C3, and C4. The calibration curves are typical of the curves developed for the elements listed above. The eight elements listed above were all easily analyzed by conventional atomic absorption techniques. The remaining six elements (As, Se, Be, Cd, Sb, and Hg) are more difficult to analyze by this technique. Each requires some special treatment; therefore, they are described separately.

C3.4.2 Special Atomic Absorption Analyses

C3.4.2.1 Arsenic (As) and Selenium (Se)

Arsenic and selenium are probably the two most difficult elements of the fourteen elements listed to analyze. Their primary resonance wavelengths are 193.7 and 196.0 nm, respectively. These wavelengths are in the vacuum ultraviolet region where almost all chemical species have at least some absorption characteristics. These absorptions and the noise associated with flickering within the flame increase the lower detection limits for these elements. Five methods of analysis were attempted:

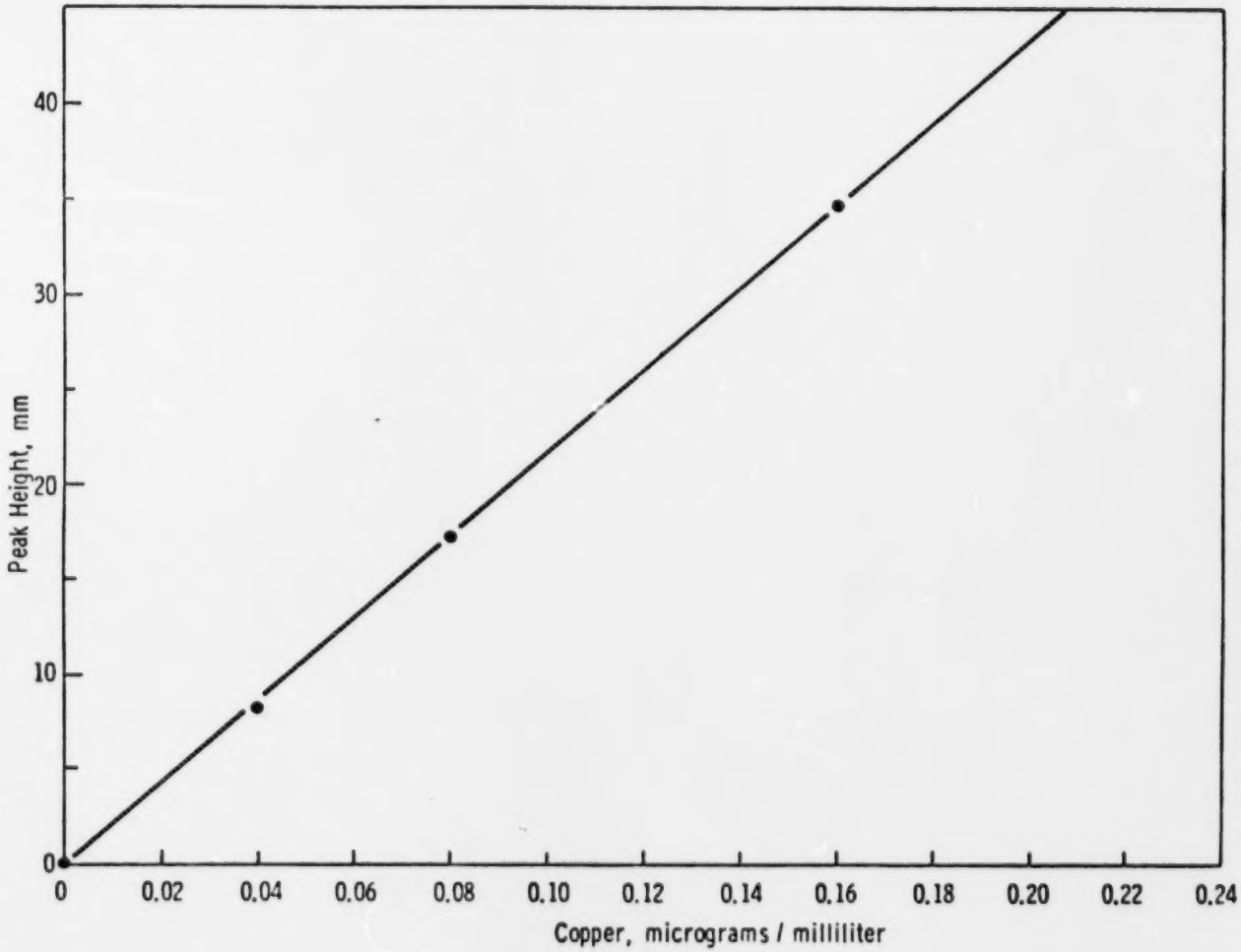

Figure C1. Atomic Absorption Calibration Curve for Cu in 25% Sulfuric Acid

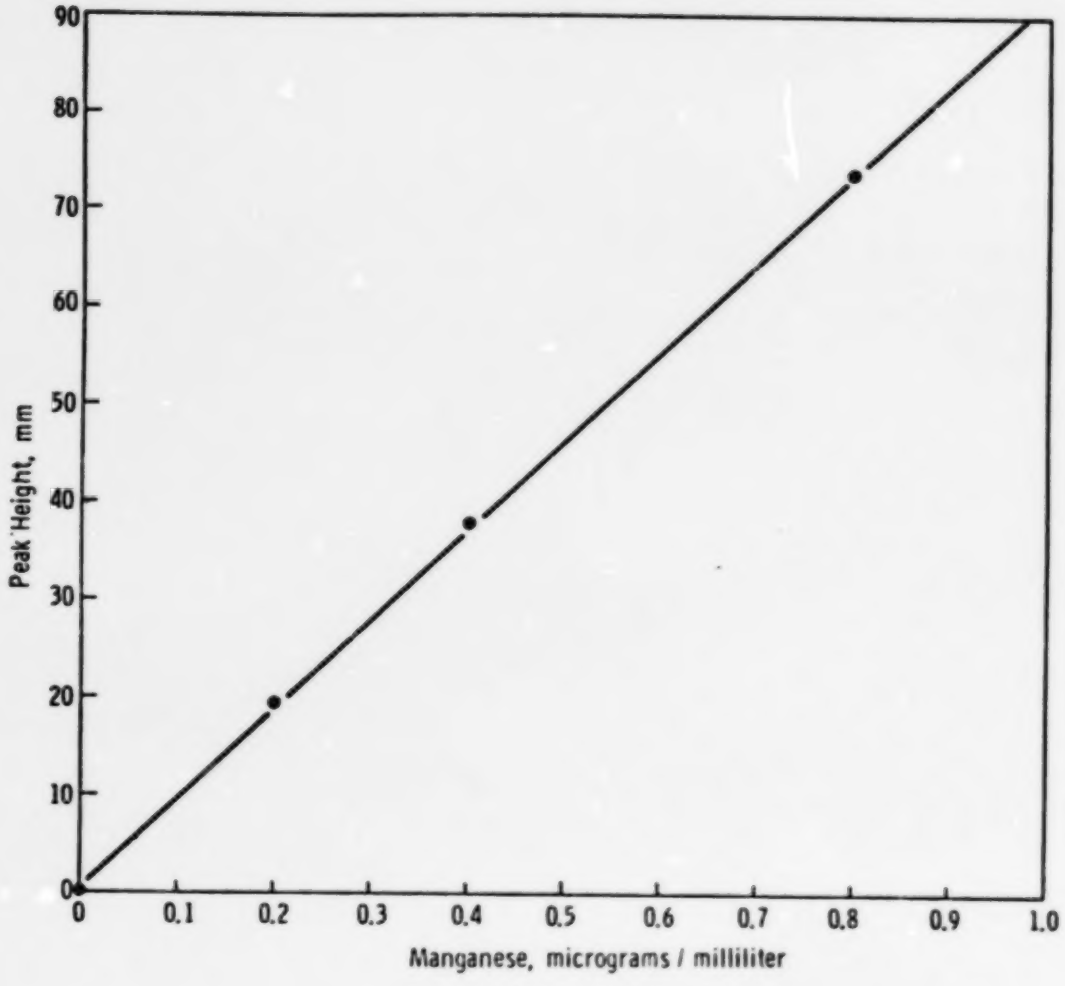

Figure C2. Atomic Absorption Calibration Curve for Mn in 25% Sulfuric Acid

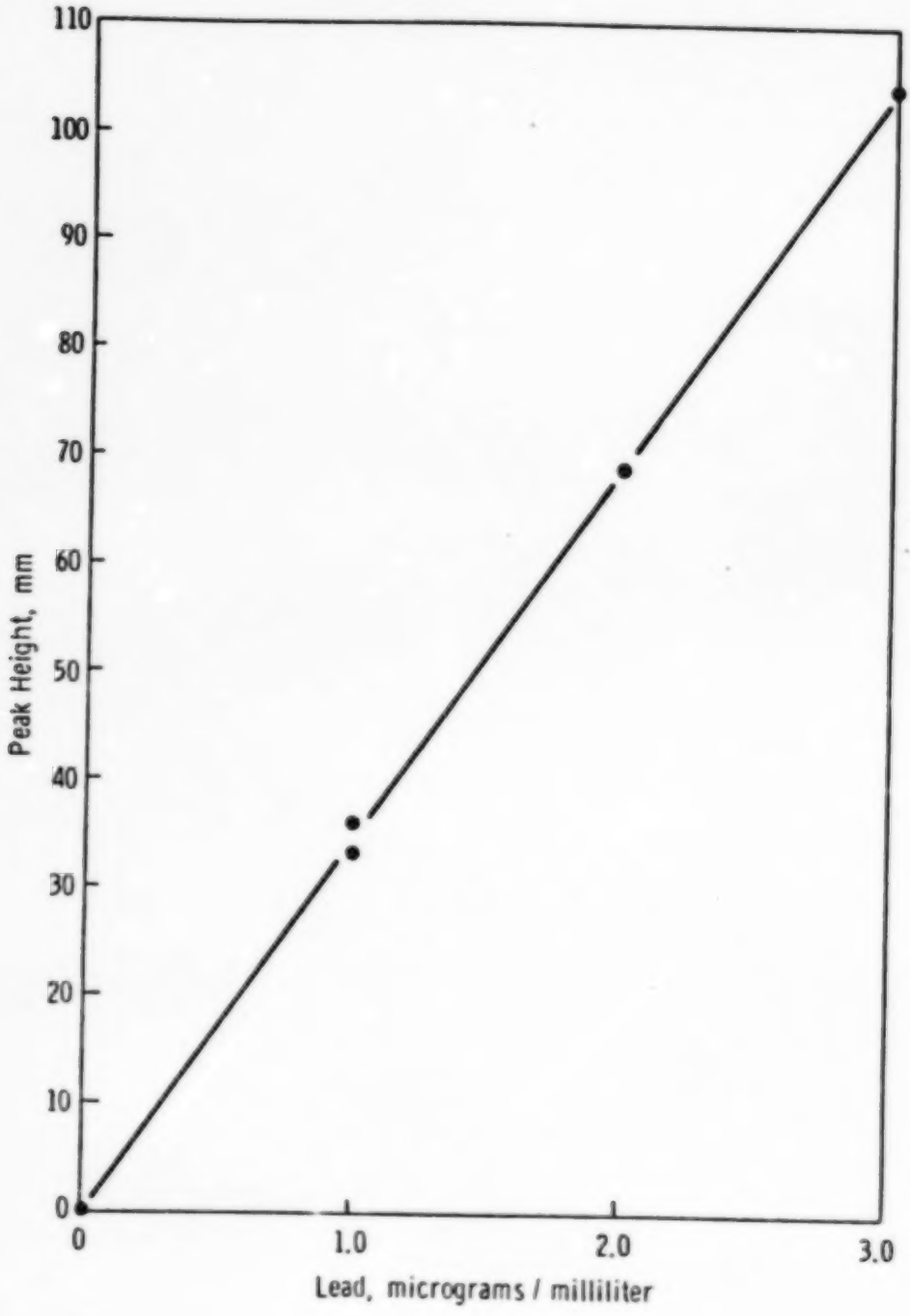

Figure C3. Atomic Absorption Calibration Curve for Pb in 25% Sulfuric Acid

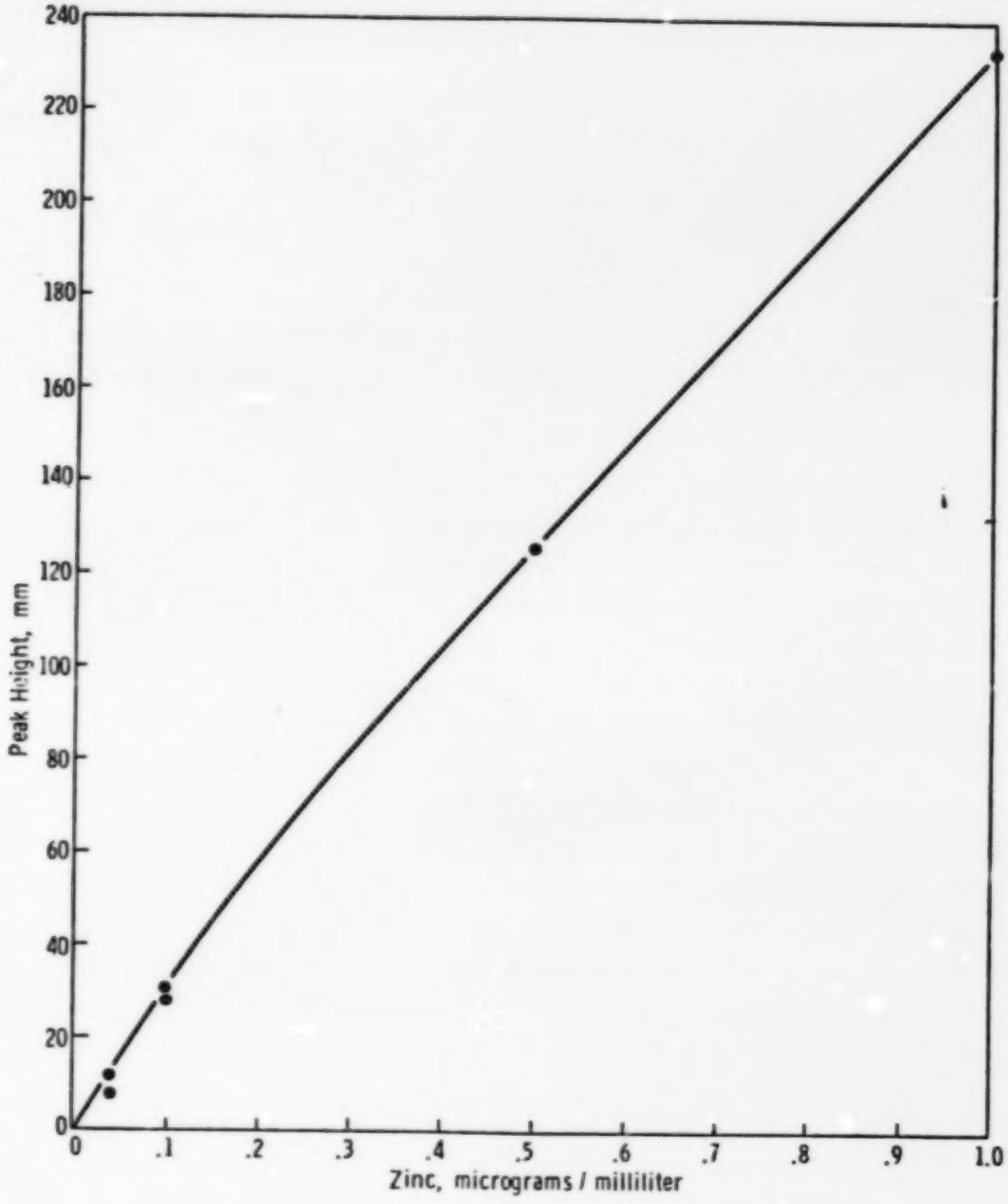

Figure C4. Atomic Absorption Calibration Curve for Zn in 25% Sulfuric Acid

1. Flame absorption - Air-acetylene flame
2. Flame Absorption - Argon-hydrogen-entrained air flame
3. Carbon Rod Atomization - (See Be and Cd analyses)
4. Hydride formation followed by flame absorption - (See Sb analyses)
5. Addition of 1 ml of 10% hydroxylamine hydrochloride to 40 ml of 25% sulfuric acid samples, standards and blanks followed by flame absorption - argon-hydrogen-entrained air flame.

In the arsenic analyses using Method 5, average signal for the samples was 15-27 mm above the average signal observed for the blank solution. However, since the width of the noise in the signal is ∿25 mm, the minimum detection limit would be ∿50 mm if the rule, that the minimum detection limit is a signal twice as large as the width of the average noise, is applied. For selenium average signal for the samples was 9.5-34 mm, average noise was 18 mm and minimum detection limit was 36 mm. Therefore, since the results were below the detection limit of the method, they will not be reported. The values obtained by ASARCO for these samples are shown in Table 4. The author recommends a solvent extraction procedure for separating As and Se from sulfuric acid be investigated. Diethylammonium diethyldithiocarbamate has been found to form quantitatively extractable chelates with As and Se from sulfuric acid samples as concentrated as 10 N[9,10,11].

The extracted chelate in an organic solvent could be analyzed by a number of techniques. The organic solvent may be atomized directly into the flame or applied to the carbon rod and analyzed by flameless absorption. The organic solvent can be evaporated and the As and Se containing chelate residue analyzed by x-ray fluorescence. By shaking the organic solvent

with a basic solution (pH > 8), the chelate is destroyed and the As and Se are transferred to the aqueous layer. This aqueous layer may then be used for flame or flameless atomic absorption. The aqueous layer could also be analyzed via a colorimetric analysis.

C3.4.2.2 Beryllium (Be) and Cadmium (Cd)

Beryllium and cadmium were analyzed using a Varian Model 61 carbon rod flameless atomic absorption atomizer power supply and a Model 63 Varian carbon rod head assembly. The reader is referred to Varian instruction manuals[5,12] for a complete description of the carbon rod assembly. The microtube furnace was used in both cases. The micro tube furnace is made of pyrolytic graphite and is sheathed from oxidation at high temperatures by a flow of argon. Extremely high atomization temperatures are obtainable with this furnace (>3000°C). The methodology for analysis of Be and Cd in strongly acid solutions had been developed by MRC on an earlier EPA contract[13]. The carbon rod assembly is used for Be analyses because the refractory nature of Be compounds requires a very high temperature to atomize the compounds. Lower detection limit for Be is 5×10^{-10} gram/milliliter using the carbon rod assembly to analyze 25% sulfuric acid samples. Dry, ash, and atomize times and voltages for Be analysis using the carbon rod assembly are shown in Table C3.

Cadmium analyses of the 25% H_2SO_4 samples and standards were performed using both an argon-hydrogen-entrained air flame for higher concentration samples and the carbon rod assembly. The lower detection limit using the flame was 1.6×10^{-8} gram/milliliter and 1×10^{-10} gram/milliliter using the carbon rod

Table C3

Instrument Operating Parameters

For a Varian Model 63 Carbon Rod Atomizer
Used with a Perkin-Elmer Model 303
Atomic Absorption Spectrometer

	Dry Cycle		Ash Cycle		Atomize	
Element	Time (sec)	Voltage (volts)	Time (sec)	Voltage (volts)	Ramp Rate	Cut-Off Voltage (volts)
Be	12	5	10	7	4	9
Cd	12	5	10	7	6	5

assembly. Operating parameters for the carbon rod are shown in Table C3. Flow rate of argon when using the carbon rod assembly was 4.5 liters/minute.

C3.4.2.3 Antimony (Sb)

Antimony was determined using a Perkin-Elmer Model 303-0849 volatile hydride generator and methods developed by Perkin-Elmer.[3,14] Forty milliliters of 25% sulfuric acid sample is reacted first with a reducing agent such as stannous chloride then with a source of nascent hydrogen. The hydrogen produced reacts with Sb to form stibine, SbH_3, a gas. The hydrogen and stibine are collected in a balloon-type reservoir after the reaction is complete, two minutes for Zn, 30 seconds for sodium borohydride. The gas is swept from the generator and reservoir to the argon-hydrogen-entrained air flame by argon. Standards, blanks and samples are all treated in the same manner. Note: Although the hydrides of arsenic and selenium can be formed in a similar manner, attempts at using this method for arsenic and selenium were not successful.

C3.4.2.4 Mercury (Hg)

The basic method for analysis of Hg is based on a procedure originally developed by Dow Chemical Company[15] for analysis of Hg in water. An aliquot of sample is placed in an erlenmeyer flask, 1 milliliter of 5% potassium permanganate is added and a watch glass is placed on the top of the flask. The sample is heated on a hot plate until the sample boils for two minutes.

After the sample is cooled to room temperature, 10% hydroxylamine hydrochloride is added dropwise to destroy excess permanganate. An aliquot of the sample is transferred to a bubbler flask and 2 ml of 40% stannous chloride in 9N hydrochloric acid is added

to the flask. This reduces all Hg present to Hg°. A flow of argon is then diverted through the bubbler and carries Hg vapor through a 10-cm gas cell in the beam of the atomic absorption spectrometer.

C3.4.3 Spectral Background Interferences from Non-Atomic Absorption

Non-atomic absorption is due to molecular absorption and/or light scattering by solid particles in the flame or other form of atomization. Molecular absorption is caused by the presence of molecular species in the flame which absorb light at the same wavelength as the element resonance line. Light scattering by particles in the flame results when solutions of high total solids are aspirated into a burner. Both types of non-atomic absorption occur over wide spectral bands (>10 nm) compared with the 0.01 nm absorption for atomic lines in the flame.

Corrections for non-atomic absorption interferences can be made by comparing the absorption at a specific wavelength obtained with a hollow cathode lamp versus the absorption values obtained with a continuum lamp (hydrogen or deuterium). The absorption measurement obtained with a hollow cathode line source is the sum of an element's atomic absorption and the non-atomic absorption. The absorption measured with the continuum lamp is, to a close approximation, the non-atomic absorption only. The sample's true atomic absorption is the absorption measured using the hollow cathode line source less the absorption measured using the continuum source.

A hydrogen continuum lamp was used to check for non-atomic absorption during the analyses described in the previous sections. No non-atomic absorption was observed for any of the elements analyzed.

C4.0 ASARCO METHODS FOR ARSENIC (As) AND SELENIUM (Se)

The methods described in this section are the procedures ASARCO normally uses for measurement of low levels of arsenic and selenium in concentrated sulfuric acid samples. MRC has not tried these methods, therefore MRC cannot substantiate the validity of these methods. The methods are reproduced exactly as submitted to MRC by ASARCO. With the selenium procedure, an additional pretreatment of "black acid" samples should be made by cautiously mixing 5 ml of 30% H_2O_2 with the H_2SO_4 aliquot in a 250 ml beaker and heating until the acid is decolorized and the H_2O_2 decomposed. After cooling, mix with the calculated amount of water in step 4 of the procedure and proceed from there.

C4.1 DETERMINATION OF ARSENIC IN SULFURIC ACID - PHOTOMETRIC Ag-DDC METHOD

Principle

Arsine is evolved with granulated zinc and hydrochloric acid and absorbed in a silver diethyldithiocarbamate-pyridine solution. The red color is measured photometrically at 540 nm.

Reagents

Standard Arsenic - Dissolve 0.132 g of arsenic trioxide (As_2O_3) in 50 mil water containing 5-6 pellets of NaOH. Transfer to a 1-liter volumetric flask and dilute to the mark with water. (1 ml = 0.1 mg As). Transfer by pipet 5.00 ml of this solution to a 100-ml volumetric flask and dilute to the marks with water. (1 ml - 0.005 mg As).

Ag-DDC - Dissolve 0.5 g of silver diethyldiethiocarbamate (Fisher #5-666) in pyridine and dilute to 100 ml with pyridine.

15% KI solution - 15 g KI dissolved in 100 ml water.

40% $SnCl_2$ solution - 40 g $SnCl_2$ dissolved in concentrated HCl. Dilute to 100 ml with concentrated HCl.

Apparatus

This procedure is written for use with a photometer employing a 2-cm cell. See Figure C5.

Range

0.001 mg to 0.25 mg As.

Procedure

Transfer a 5 ml aliquot (∿9.2 g) of the sulfuric acid sample to a 125 ml Erlenmeyer flask. Add cautiously 5 ml HNO_3 and heat to dense fumes. If charring of any organics present begins to occur, add additional HNO_3 to prevent any losses of arsenic. Heat to dense fumes. Cool to room temperature. Wash down walls of flask with a small amount of water and refume. Cool. Add 50 ml of water and cool again. Add 10 ml HCl.

Add 2 ml of 15% KI solution and then decolorize with 1 ml of $SnCl_2$ solution. Let stand at room temperature 15-20 minutes. Assemble the apparatus. Have the 15 ml of Ag-DDC solution in the tall graduate ready. Quickly add 5.0 gm of 40 mesh granulated Zn (low in As), restopper the flask and evolve arsine for 20-30 minutes.

Disconnet apparatus, transfer Ag-DDC pyridine solution to a dry photometer tube and determine % T. at 540 nm. Calculate % As. Run blanks through entire procedure. Large amounts of Sb interfere Sb reads ∿8% of the As.

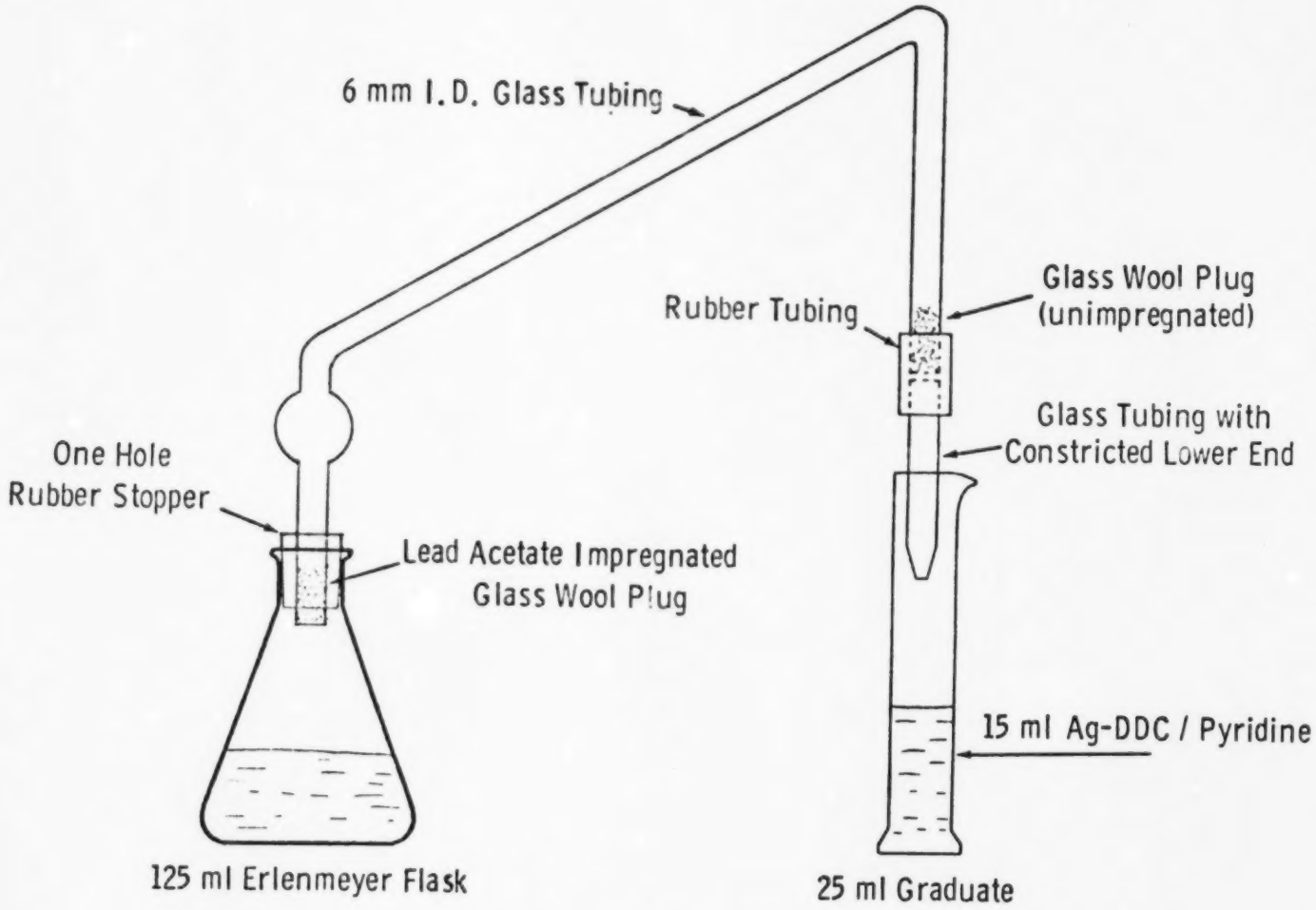

Figure C5. Arsine Evolution Apparatus

Calibration

Transfer 0.0, 1.0, 2.0, 3.0 and 5.0 ml of Standard Arsenic Solution (1 ml = 0.005 mg As) to each of five 125-ml Erlenmeyer flasks, respectively. Add 50 ml water, 5 ml H_2SO_4 and 10 ml HCl to each flask, cooling between additions. Add 2 ml of 15% KI solution, and 1 ml of 40% SnCl in HCl. Let stand 15-20 minutes.

Transfer 15.0 ml of Ag-DDC solution to a 25-ml graduate. Add 5 g of 20 mesh zinc and quickly assemble the apparatus. After 20-30 minutes, disassemble and transfer the absorbing solutions to photometer tubes and measure photometrically. Plot mg As versus transmittance on semi-log paper (Figure C6).

C4.2 COLORIMETRIC DETERMINATION OF Se IN SULFURIC ACID

Principle

A 50-ml aliquot of the sulfuric acid is diluted with enough water to give a 6 normal solution. An amount of ammonium chloride equivalent to the amount of H_2SO_4 present is added, yielding a solution that is 6BN in H^+ and Cl^-. An arsenic separation is done on this solution, and the Se determination is completed in the usual manner.

Procedure

1. If the normallity of the H_2SO_4 is unknown, determine it by titrating a 1.0-ml aliquot with 1N NaOH, using methyl orange or any other appropriate indicator. The reading on the buret will be the normality of the acid.

Example: A 35.0 ml reading is equivalent to 35.0 N acid.

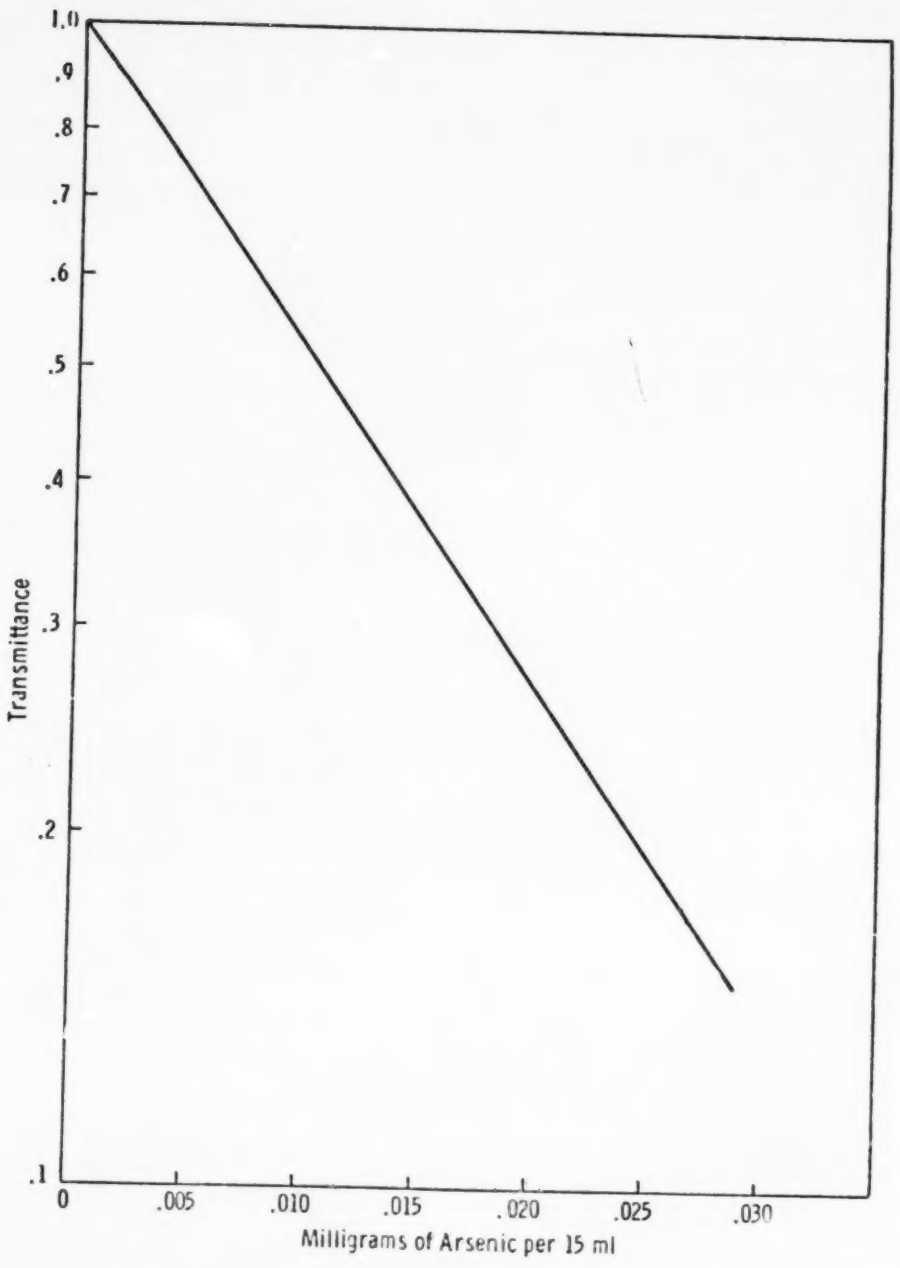

Figure C6. Arsenic Calibration Curve

2. Calculate the volume to which 50 ml of the acid must be diluted to give a 6N solution, using the formula ml x N = ml x N.

Example: (for 35.0 N H_2SO_4)
50 x 35.0 = ml x 6
vol. = 292 ml

3. With a graduated cylinder measure a volume of distilled water about 100 ml less than that calculated in Step 2 and add it to a 800 ml beaker.

4. Add 50.0 ml of the H_2SO_4 to the distilled water by pipet, swirling the tip of the pipet in the water and cooling, if necessary, to prevent the water from boiling excessively.

5. Sometimes H_2SO_4 samples contain SO_2. If there is any odor of SO_2 in the sample, boil the solution from Step 4 until no more odor of SO_2 can be detected. (If this is not done, the SO_2 will react with the hypophosphorus acid in step 8 to form sulfur).

6. Calculate the weight of NH_4Cl that will be equivalent to 50 ml of the acid.

Example: Normality x liters = number of equivalents
No. of equivalents x equivalent wt. of NH_4Cl = grams of NH_4Cl

35.0 x .050 = 1.75 equivalents
1.75 x 53.8 = 94.2 grams of NH_4Cl

7. Add the NH_4Cl to the 800 ml beaker and add enough hot distilled water to bring the volume up to that calculated in Step 2. (Sometimes it is necessary to add a little more water to get all the NH_4Cl into solution, especially if the acid is strong.)

8. Add 5 ml of arsenic solution (1.0 mg As/ml) and 25 ml of hypophosphorous acid to the 800 ml beaker. Cover, place on the hot place, and boil for 10 minutes.

9. Remove from the hot plate and add 50 ml of H_2O. Cool and filter through a No. 42 filter paper or a 1.2μ Millipore. If NH_4 salts come out during the filtration, add a little hot water.

10. Finish the Se determination in the usual manner.

11. Calculate the ppm Se in the H_2SO_4 according to the formula:

$$\frac{\text{mg Se}}{.050 \times \text{sp.gr. of } H_2SO_4} = \text{ppm Se}$$

C.4.3 COLORIMETRIC DETERMINATION OF SELENIUM AND TELLURIUM

Discussion

The following methods for Se and Te both begin in the same way: The sample dissolution is the same for both and both are separated from other constituents by an arsenic co-precipitation. If a substance is to be analyzed for both Se and Te, a single sample can often be used as the starting point for both determinations, at a great saving of time and effort. This is done by dissolving the arsenic precipitate containing the Se and Te and diluting it to 100 mls. Then appropriate sized aliquots are drawn for Se and Te and the determinations completed individually.

SELENIUM

Application

The method applies to the analysis of concentrates, matte, speiss, slags, dusts, sinters, calcines, blister copper, anode copper and copper tankhouse electrolytes. For the determination of Se

in cathode copper, lead bullion, refined lead, arsenic, tellurium; etc., and solders, see methods applying specifically to these substances.

The Method in Brief

The sample is decomposed with HNO_3, HF, and $HClO_4$. The first two acids and SiO_2 are expelled by taking to $HClO_4$ fumes. The resulting mixture is taken up with 1:1 HCl, arsenic solution is added, and the Se (together with any Te present) co-precipitated with the As by reduction with hypophosphorous acid. The arsenic precipitate is dissolved and treated with 3,3'-diaminobenzidine at pH 2-3. The intensely yellow-colored compound of Se and diaminobenzidine is extracted with toluene at pH 8 and measured photometrically at 420 mμ.

Interferences

This method is specific for Se. There are no known interferences.

Reagents

Arsenic Solution - Dissolve 0.25 g of arsenious oxide (As_2O_3) plus 10 pellets of NaOH in 10 ml of distilled water by warming. Dilute to 200 ml and mix.

META Cresol Purple Indicator Solution (MCP) - Dissolve 0.10 g of meta cresol purple plus 1 pellet of NaOH in 10 ml of distilled water by warming. Dilute to 100 ml and mix.

EDTA Solution (2%) - Dissolve 20.0 g of disodium ethylenediaminetetraacetate, dihydrate, in 900 ml of distilled water. Dilute to 100 ml and mix.

Formic Acid Solution (1:9) - Mix 20 ml of formic acid with 180 ml of distilled water.

Diaminobenzidine Solution (0.5%) - Dissolve 0.100 g of 3,3'-diaminobenzidine (tetra) hydrochloride in 20 ml of distilled water. Prepare fresh daily and store under refrigeration. Only enough solution should be prepared at a time as will be used immediately, as the reagent in aqueous olution is not very stable and is quite costly.

Standard Selenium Solution (1 ml = 0.02 mg Se) - Dissolve 0.5000 g of high purity selenium in 20 ml of nitric acid and boil to expel oxides of nitrogen. Cool and dilute to 500 ml with distilled water and mix. Transfer a 10.0-ml aliquot to a 500 ml volumetric flask, dilute to volume and mix. 1 ml = 0.02 mg Se.

Preparation of Calibration Curve

(a) Transfer 0.00, 0.50, 1.00, 2.00, 3.00 and 4.00 ml of standard selenium solution (1 ml = 0.02 mg Se) to each of six 250 ml copper assay flasks respectively, using Mohr pipettes. (3) To each flask add 3 ml of $HC1O_4$ and evaporate to not less than 2 ml volume. Cool somewhat, add 50 ml of distilled water, and boil for about 1/2 to 1 minute. Cool to room temperature.

(b) Add 5.0 ml of 2% EDTA solution and 2 drops of MCP indicator solution. Neutralize with NH_4OH dropwise just to the yellow color of the indicator. (2) Add 2.0 ml of formic acid (1:9) and 2.0 ml of freshly prepared diaminobenzidine solution. Heat for 5 min. in a boiling water bath. A 600 ml beaker with approximately 200 ml of water makes an ideal bath. Cool to room temperature.

(c) Neutralize with concentrated ammonium hydroxide dropwise to the purple color of the indicator pH = 8 (11-12 drops of conc. NH_4OH are required.) Pour each solution into a 125 ml separatory funnel. (3) Drain well but do not wash. From a

burette, add 12.0 ml of toluene, stopper and shake vigorously for 30 seconds. Allow the layers to separate and drain and discard the lower aqueous layers. Filter the organic layers through dry, folded, 9 cm Whatman No. 41 H papers into colorimeter tubes. Measure at 420 mμ against the reference blank.

(d) Plot the photometer readings against milligrams of selenium on semi-logarithmic paper.

Procedure

Transfer a 1-g sample (1) to a 250 ml copper assay flask (3). Add 10 ml of HNO_3, 5 ml of $HClO_4$, and 4-6 drops of HF (1-2 ml of HF for slags). Heat on a hot plate until brown fumes have subsided, then swirl the flask over a Meker burner until heavy fumes of $HClO_4$ appear. If beads of sulfur remain, set the flask on the hot plate until they are oxidized or burn off. Cool somewhat. Add 3-4 ml of water and swirl to break up the cake. Add 100 ml of 1:1 HCl, 2 ml of arsenic solution, and 1 or 2 Hengar granules. Mix. (If a clear solution is not obtained at once, the solution may be warmed, but should not be boiled.) Add 15 ml of 50% hypophosphorous acid (H_3PO_2) and swirl to mix. Place the flask on the hot plate and simmer gently for approximately 10 minutes until the arsenic precipitate coagulates. CAUTION: Do not allow any of the solution to splash or leak on to the hot plate (4). After the precipitate has coagulated, cool to about 70°F by allowing the flask to stand on the bench top for 10-15 minutes (5).

Filter the warm solution through an 11 cm Whatman No. 42 filter paper. Wash the flask three times with a hot solution of 1-1 HCl containing about 3-4 ml of H_3PO_2 per 100 ml of solution, pouring the washings into the filter. Wash the paper two additional times with small portions of the HCl-H_3PO_2 wash

solution. Wash the flask three times with small portions of hot distilled water, pouring the washings into the filter. Wash the paper 10 additional times with small portions of hot distilled water. Test this water coming out of the funnel with pH paper; if it is still acid, continue washing until it is neutral.

Transfer the paper and precipitate back to the original flask. Wipe out the funnel with a small piece of damp filter paper to gather any precipitate adhering to the funnel and add to the flask. Add 10 ml of nitric acid and 5 ml of perchloric acid to the flask. Place the flask on the hot plate and boil until the paper is destroyed (6). Swirl the flask over the Meker burner until dense fumes of perchloric acid appear, but do not evaporate to less than 2 ml. Cool somewhat, add 50 ml of distilled water and boil for 1/2 to 1 minute. Cool to room temperature. (If the Se in the sample is higher than 0.007%, dilute to volume and pipet an aliquot (1). Add enough distilled water to the aliquot to bring it up to 50 ml).

Prepare a blank from 10 ml of HNO_3 and 5 ml of $HClO_4$ fumed down to 2 ml in a copper assay flask. Add 50 ml of distilled water and boil for 1/2 to 1 minute. Cool to room temperature.

Continue in accordance with paragraphs (b) and (c) under Preparation of Calibration Curve.

By referring to the calibration curve, determine the milligrams of Se present and compute the percentage of Se in the sample:

$$\frac{\text{Milligrams of Se}}{\text{grams of sample x 10}} = \% \text{ Se}$$

Notes

(1) The useful range of the colorimetric curve is from about 0.005 mg Se to about 0.07 mg Se. For a 1-g sample, this corresponds to 0.0005% Se to 0.007% Se. If the Se present in the sample is in the 0.005% to 0.07% range, use a 1-g sample but dilute the dissolved arsenic precipitate to 100 ml in a volumetric flask and pipet a 10 ml aliquot. This corresponds to a 0.1 g sample.

If the Se present is in the 0.05% to 0.7% range, use a 1-g sample but dilute the arsenic precipitate to 500 ml in a volumetric flask and pipet a 5 ml aliquot, corresponding to a 0.01-g sample. Amounts of Se higher than 0.5% are within the range where they can be done by atomic absorption which is much faster and easier.

Samples of copper tankhouse electrolyte need not be given the preliminary decomposition with HNO_3, $HClO_4$, and HF, but may be combined directly with the 100 ml of 1:1 HCl.

(2) The indicator color at this point must be just barely yellow, so that when the formic acid is added, the color will change from yellow to orange or pinkish-orange.

(3) A set of flasks and separatory funnels should be cleaned thoroughly and set aside for use only in this selenium determination to avoid contamination. It should be kept in mind, however, that repeated use with HF results in gradual erosion of the copper assay flasks and the development of thin spots, especially on the bottom. Cases are known where thin copper assay flask have developed leaks while on the hot plate resulting in loss of samples and even explosions (See Note 4). To avoid this, it is

essential that the copper assay flasks be tested prior to each use by tapping the bottoms on a pointed wooden object such as the corner of a beaker tray or cabinet door. This treatment will crack or break flasks with thin bottoms.

(4) If the solution containing hypophosphorous acid and perchloric acid should leak, bump, or be spilled so that the solution comes into direct contact with the hot plate, spontaneously flammable phosphine is formed. With the oxidant, concentrated perchloric acid, also present, a small but violent explosion may result.

For this reason, the solutions should not be boiled hard, one or two Hengar granules should be present, and flasks with thin bottoms should not be used.

(5) Cooling to about 70°C is mandatory; if the 1:1 acid solution is much hotter than 70°C, the filter paper may break.

(6) Destruction of filter paper with HNO_3 and $HClO_4$ is done by boiling the mixture at a moderate (not fast) rate. Oxidation of the last traces of organic matter occurs in about 10 - 15 minutes and is indicated by a rather sudden onset of vigorous bubbling. The bubbling subsides in 5 - 10 seconds leaving a colorless solution of $HClO_4$ which may then be fumed over a Meeker burner. If, instead of bubbling, the solution turns suddenly dark, more HNO_3 should be added. The need for this arises only when the HNO_4, $HClO_4$ and the paper are boiled too fast.